



Aalborg Universitet

AALBORG UNIVERSITY
DENMARK

AMMONOX-Ammonia for enhancing biogas yield & reducing NOx.

Gavala, Hariklia N.; Kristensen, P.G. ; Paamand, K. ; Thostrup, P. ; Skiadas, Ioannis

Published in:

Proceedings of the 13th World Congress on Anaerobic Digestion: Recovering (bio) Resources for the World, Santiago de Compostela, Spain, June 25-28

Publication date:

2013

Document Version

Accepted author manuscript, peer reviewed version

[Link to publication from Aalborg University](#)

Citation for published version (APA):

Gavala, H. N., Kristensen, P. G., Paamand, K., Thostrup, P., & Skiadas, I. (2013). AMMONOX-Ammonia for enhancing biogas yield & reducing NOx. In *Proceedings of the 13th World Congress on Anaerobic Digestion: Recovering (bio) Resources for the World, Santiago de Compostela, Spain, June 25-28* IWA Publishing. <http://www.ad13.org>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal -

Take down policy

If you believe that this document breaches copyright please contact us at vbn@aub.aau.dk providing details, and we will remove access to the work immediately and investigate your claim.

AMMONOX-Ammonia for enhancing biogas yield & reducing NO_x

H.N. Gavala*, P.G. Kristensen**, N.B.K. Rasmussen**, P. Thostrup***and I.V. Skiadas*

* Aalborg University Copenhagen (AAU-Cph), Department of Biotechnology, Chemistry and Environmental Engineering, Section for Sustainable Biotechnology, A C Meyers Vænge 15, DK 2450 Copenhagen SV Denmark (E-mail: ivs@bio.aau.dk; hmg@bio.aau.dk)

** Danish Gas Technology Centre, Dr. Neergaards Vej 5B, DK-2970 Hørsholm, Denmark

*** Nordic BioEnergy ApS, Jelshøjvænget 11, 8270 Højbjerg, Aarhus, Danmark

Abstract

The continuously increasing demand for renewable energy sources renders anaerobic digestion to one of the most promising technologies for renewable energy production. Due to the animal production intensification, manure is being used as the primary feedstock for most of the biogas plants. However, biogas plants digesting liquid manure alone are not economically viable due to the relatively low organic content of the manure, usually 3-5%. Thus, their economical profitable operation relies partly on increasing the methane yield from manure, and especially of its solid fraction, usually called as 'manure fibers', which is not so easily degradable.

Laboratory tests have shown that ammonia is very effective for the pre-treatment of manure fibers and other lignocellulosic biomasses but also for the post-treatment of manure fibers after anaerobic digestion (digested manure fibers). It has to be emphasized that apart the increased methane yield, the ammonia used can be recovered and recycled from the liquid manure resulting in no consumption of chemicals and actually in production of excess ammonia.

AMMONOX is an innovative concept focusing on an integrated approach for sustainable and cost-efficient energy production in the form of methane from manure. The three pillars of AMMONOX are a) the optimisation and application of Aqueous Ammonia Soaking (AAS) as a moderate and sustainable chemical treatment for enhanced methane production from manure fibers and lignocellulosic biomasses, b) the application of innovative ammonia recovery technology and c) the coupling of the excess ammonia obtained from manure with the catalytic elimination of NO_x emissions when the biogas is used for subsequent electricity generation with gas engines.

Keywords

Aqueous Ammonia Soaking; methane; NO_x reduction; AMRECO; RETROMAX; manure; lignocellulose

INTRODUCTION

In recent years, biogas technology has progressed rapidly and its application has experienced an explosive growth worldwide, with electricity from biogas playing an integral part of the global energy market (UNEP, 2008). Currently, most agricultural biogas plants are used to ferment liquid manure (Deublein and Steinhauser, 2008) due to several advantages. Anaerobic digestion is a spontaneous process based on microorganisms already existing in manure. Additionally, production of biogas from manure results in much higher reduction in greenhouse gas emission than other biofuels producing processes and equal savings in fossil fuels. As cost aspects point to the same direction, manure based biogas should have higher priority from other biofuels (Thyø and Wenzel, 2007). The potential for heat and electricity from biogas in Denmark is at least 10 times higher than it is produced today. This potential is based mainly on manure. On the other hand, manure biogas efficiency is poor due to its relatively low organic content and therefore biogas plants digesting liquid manure alone are not economically viable. Current biogas production in Denmark is based on mixing manure with other (additional) biomasses characterized by higher methane potential, such as slaughterhouse wastes, glycerine, crops, animal fat, fish oil, etc. However, due to the increased demand for biomass feedstock in the bio-energy sector, the supply of these additional biomasses is

becoming increasingly limited or expensive.

The alternative option is to use lignocellulosic biomasses such as manure fibers and agricultural and forest residues, which, however, need to be pretreated in order to be efficiently converted to methane. The existing pretreatment methods are based on high temperature and pressure and/or use of harsh chemicals and thus they increase significantly the cost of biogas/electricity production. Ammonia is among the chemicals that can be used biomass pretreatment. Also, ammonia is a chemical which exists at relatively high concentrations in manure effluents. As such, it negatively affects the environmental performance of biogas plants and quite often it can significantly reduce the methane efficiency due to inhibition of biological processes.

A relatively simple pretreatment method based on ammonia with minimal process technology requirements (no high temperature and pressure) is aqueous ammonia soaking (AAS). AAS has been used to increase the digestibility of low quality forages and crop residue in ruminants (Hashimoto, 1986). Streeter and Horn (1980) reported that the digestibility of crop residues treated with 24% ammonia was generally increased and they assumed that ammonia could dissolve hemicellulose and thereby increase the accessibility of cellulose. AAS has been applied lately to different lignocellulosic biomasses mainly for bioethanol or other organic solvents. So far, AAS has been tested in laboratory or pilot scale for bioethanol and chemicals production and has given interesting results but its efficiency is significantly lower than that of other (high temperature and pressure) thermochemical pretreatment methods, which is translated to increased use of enzymes at the subsequent stages. On the other hand, anaerobic digestion of manure or other biomasses does not require the production of a medium with high concentration of soluble sugars in order to be efficient because the microbial consortium performing anaerobic digestion has the ability to produce all the necessary enzymes for the hydrolysis of cellulose and hemicellulose. Despite the advantages of AAS and the low requirements of the anaerobic digestion process, studies on the effect that AAS has on methane production from various lignocellulosic biomasses were scarce with just those of Hashimoto (1986) (straw) and Himmelsbach et al. (2010) (switchgrass) found in the international literature until recently.

Based on the very promising results obtained so far and discussed in the sequel, an innovative concept, AMMONOX, for renewable, sustainable and cost-efficient energy production in the form of methane from manure was proposed and received support for further development. The three pillars of AMMONOX are a) the optimisation and application of AAS as a moderate and sustainable chemical treatment for enhanced methane production from manure fibers and lignocellulosic biomasses, b) the application of innovative ammonia recovery technology and c) the coupling of the excess ammonia obtained from manure with the catalytic elimination of NO_x when the biogas is used for subsequent electricity generation with gas engines. In the sequel, the three pillars of AMMONOX are presented along with representative results from AAS of manure fibers.

AMMONOX-PROCESSES INVOLVED AND MAJOR RESULTS OBTAINED

Aqueous Ammonia Soaking (AAS) of manure fibers and methane enhancement

Experimental methodology. Raw and digested (before and after anaerobic digestion, respectively) manure fibers were collected at a mesophilic biogas plant treating manure and manure fibers (Morsø BioEnergi.). Manure fibers were soaked in ammonia reagent at a ratio of 10 mL reagent per g TS. After the completion of the treatment, ammonia was removed by distillation in a rotary evaporator (Buchi RII Rotavapor) with a vertical condenser. Determination of methane yield enhancement under different conditions (reagent concentration in ammonia, duration, temperature) was performed in batch tests and confirmed in continuous reactors digesting a mixture of manure and AAS-treated manure fibers.

Major results obtained. The highest increase in methane yield achieved was 178% and 237% from raw and digested manure fibers, respectively, in batch tests. AAS was applied at 22°C and for 3

days while the reagent concentration in ammonia was 32% and 25% for raw and digested fibers, respectively. Specifically for digested fibers, it was found that different reagent concentration at the range of 5-25% w/w in ammonia did not affect significantly the overall methane yield, while treatment with 32% reagent concentration in ammonia resulted at approximately 14% lower methane production (Jurado et al., 2012a; Mirtsou-Xanthopoulou et al., 2012a).

Experiments in CSTR fed with manure and subsequently with a mixture of manure and AAS-treated fibers confirmed the increased methane yield. Specifically, the methane yield of AAS-treated digested fibers was calculated to be 0.24 l CH₄ / g TS in continuous experiments compared to 0.19-0.22 l CH₄ / g TS obtained in batch tests. AAS-treated raw manure fibers yielded 0.23 l CH₄ / g TS in continuous experiments compared to 0.18-0.32 l CH₄ / g TS obtained in batch tests with different TS loading (Jurado et al., 2012b; Mirtsou-Xanthopoulou et al., 2012b). It is remarkable that the ultimate methane potential of non AAS-treated raw and digested fibers was 0.117±0.009 and 0.077-0.090 l CH₄ / g TS, respectively, in batch tests (Jurado et al., 2013).

Ammonia recovery – the RETROMAX process

Anaerobic digestion can be severely inhibited by high ammonia concentrations and therefore an efficient ammonia removal step is necessary before anaerobic digestion of AAS treated biomass.

The AMRECO process (pending PCT/DK2007/000447) is going to be developed and implemented within AMMONOX. The AMRECO process uses chemical precipitation (and thus removal) of NH₄⁺ with phosphate PO₄³⁻ and Mg²⁺ in the form of struvite and regeneration and reuse of magnesium/phosphate salts. This process is relatively simple and has been successfully tested with reject water from dewatering of sewage sludge and landfill leachates. AMRECO process consists of 2 chemical process steps, both being in the same reactor initially containing magnesium phosphate. The first step is the addition of the ammonia rich liquid and the struvite precipitation. After all the ammonia has precipitated as struvite, the liquid in the reactor is extracted by vacuum filtration. The process is repeated until all magnesium phosphate has reacted and thus is unable to remove more ammonia. During the second step of AMRECO process the struvite precipitate (occupying a relatively very small volume since all the liquid content has been removed in the previous step) is heated up to 70-80°C resulting in the release of ammonia (NH₃) in the gas phase and the regeneration of magnesium phosphate. The released NH₃ is compressed at 10 bars and stored in liquid form. When regeneration phase is terminated the AMRECO reactor containing magnesium phosphate can be reused by starting up again the first step. The magnesium phosphate regeneration efficiency is very high (around 99%) eliminating the consumption of chemicals. The AMRECO process needs a particle free solution before ammonia can be recovered; therefore, the solids have to be removed after the AAS treatment. The process combining solids separation with AMRECO is called 'RETROMAX' (EUDP 2011) and is going to be implemented in the frame of AMMONOX project.

AMMONOX – THE CONCEPT

An overview of the AMMONOX concept is shown in figure 1. Part of the ammonia produced during the RETROMAX process will be recycled and reused in the AAS treatment. Since manure is rich in ammonia the RETROMAX process will be able to produce the necessary excess ammonia also for the reduction of NO_x emissions by the use of Selective Catalytic Reduction (SCR) catalysts, which is a mature and commercially available technology (Li et al., 2011 and <http://www.ihl.co.jp/denryoku/denox.htm>). Finally, there may be a possibility that the produced ammonia is more than enough to cover the needs of the AAS treatment and of the SCR catalysts. In such a case, the surplus of ammonia can easily be converted in to N-fertilizer increasing the income of the biogas plant. It is anticipated that the methane increase will also cover the additional cost for the AAS and RETROMAX processes, however, a complete energy balance and cost analysis is within the primary objectives of AMMONOX project.

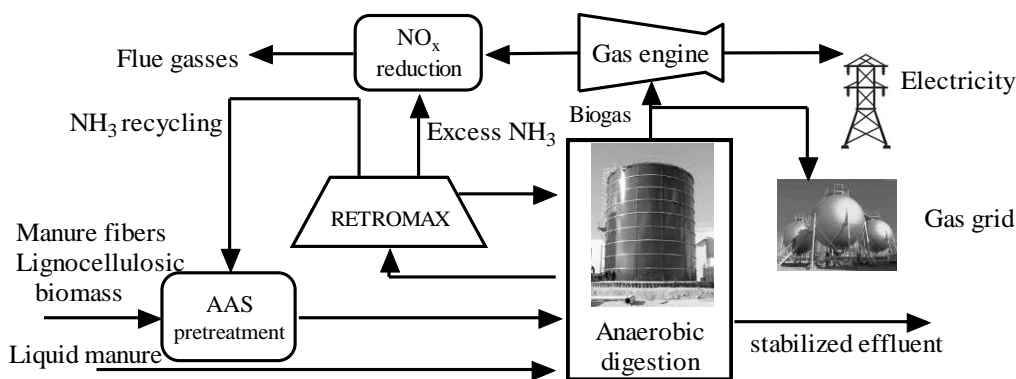


Figure 1. An overview of the AMMONOX concept.

The enhancement of methane production from manure fibers coupled to the RETROMAX process for removal and recycling of ammonia and to the selective catalytic reduction of the NO_x is a unique combination that may significantly contribute to a more sustainable and environmentally friendly electricity production from biogas. Moreover, AMMONOX will result to the economic viability of biogas plants based solely on manure by increasing the methane produced per mass of biomass treated.

ACKNOWLEDGEMENTS

The authors wish to thank the EUDP-2008, Energistyrelsen, Copenhagen for the financial support of part of this work under RETROGAS project (2009-2012) and Energinet for funding AMMONOX project (2013-2016).

REFERENCES

- Deublein, D., Steinhauser, A. 2008 Biogas from Waste and Renewable Resources. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Hashimoto, A.G. 1986 Pretreatment of Wheat Straw for Fermentation to Methane, *Biotechnology and Bioengineering*, 28, 12, 1857-1866.
- Himmelsbach, J., Raman, D., Anex, R., Burns, R., Faulhaber, C. 2010 Effect of ammonia soaking pretreatment and enzyme addition on biochemical methane potential of switchgrass. *Transactions of the ASABE*. 53, 1921-1927.
- Jurado, E., Gavala, H.N., Skiadas, I.V. 2012a Application of Aqueous Ammonia Soaking for enhancement of methane potential of swine manure fibers, *Proceedings of the 4th International Conference on Engineering for Waste and Biomass Valorisation*.
- Jurado, E., Gavala, H.N., Skiadas, I.V. 2012b ADM1-based modeling of anaerobic digestion of swine manure fibers pretreated with aqueous ammonia soaking. *Proceedings of the 4th International Symposium on Energy from biomass and Waste*.
- Jurado, E., Skiadas, I.V., Gavala, H.N. 2013 Enhanced methane productivity from manure fibers by aqueous ammonia soaking pretreatment. *Applied Energy*, 109, 104-111.
- Li, J.H., Chang, H.Z., Ma, L., Hao, J.M., Yang, R.T. 2011 Low-temperature selective catalytic reduction of NO_x with NH₃ over metal oxide and zeolite catalysts-A review. *CATALYSIS TODAY*, 175, 1, 147-156.
- Mirtsou-Xanthopoulou, C., Jurado, E., Skiadas, I.V., Gavala, H.N. 2012a Aqueous Ammonia soaking of digested manure fibers: effect of ammonia concentration and treatment duration on methane production. *Proceedings of the 4th International Conference on Engineering for Waste and Biomass Valorisation*.
- Mirtsou-Xanthopoulou, C., Jurado, E., Skiadas, I.V., Gavala, H.N. 2012b On the effect of aqueous ammonia soaking pretreatment on batch and continuous anaerobic digestion of digested swine manure fibers. *Proceedings of the 4th International Symposium on Energy from biomass and Waste*.
- Streeter, C.L., Horn, G.W. 1980 Crop Residue Management in Livestock Production and Conservation Systems, Research Report P-795, Agricultural Experiment Station, Oklahoma State University, Stillwater, OK.
- Thyø, K.A., Wenzel, H. 2007 Life Cycle Assessment of Biogas from Maize silage and from Ma-nure - for transport and for heat and power production under displacement of natural gas based heat works and marginal electricity in northern Germany Institute for Product Development: Xergi A/S, Denmark; http://www.xergi.com/images/stories/pdf/life_cycle_assessment_report.pdf (accessed 13 April 2011).
- UNEP, 2008, Global Trends in Sustainable Energy Investment 2008 Report, Executive summary, p. 2.
- EUDP, 2011, Retromax - Slurry treatment making biogas plants and farm fertilization profitable, Project number: 64011-0332